# Dendrite Growth Morphology Modeling in Liquid and Solid Electrolytes

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**Project ID: ES328**

# *Overview*

## Timeline

- Project start date: 01/01/2017
- Project end date: 12/31/2019
- Percent completed: 10%

## Barriers

Li metal film electrodes with

- Dendrite growth
- Low coulombic efficiency
- Short calendar and cycle life

## Budget

- Total project funding: $1,135,125
  - DOE share: $999,943
  - Contractor share: $135,182

## Partners

- Interactions/collaborations
  - Gary Rubloff (UMD) : Coating development
  - Katherine Jungjohann : SNL-ALBQ In situ TEM, liquid cell
- Project lead, Yue Qi (MSU)

# *Relevance / Objectives*

## *Overall Objective*

- Develop a validated multi-scale model to predict Li dendrite morphology evolution in both liquid and solid electrolytes LIBs during electrodeposition and stripping, in order to ***accelerate the adoption of Li metal electrodes in current and emerging battery technologies.***

## *Technical Target*

- An atomically-informed, fully-coupled electrochemical-mechanical dendrite morphology evolution model that allows us to design the desired properties of artificial SEI coatings, the microstructure of solid electrolyte materials, and the corresponding battery operating conditions, so as to avoid dendrite growth during cycling.

## *Impacts*

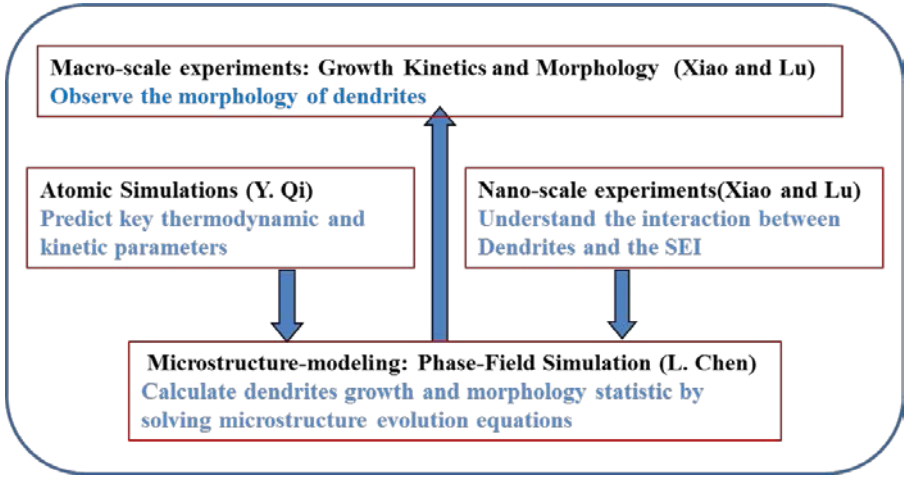
- Enable the design of durable and safe Li-anodes for high energy density Li-ion batteries that can meet DOE's target for EV applications >350 Wh/kg & <\$100/$kWh_{use}$.

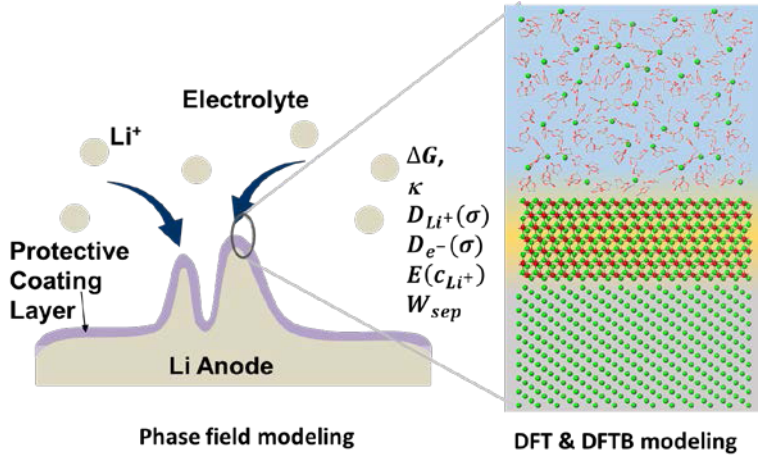
# *2017 Milestones*

| Month /Year | Milestone of Go/No-Go Decision | Status |
|---|---|---|
| Mar. 2017 | Key transport properties of SEI and (at least) one Li/SEI/electrolyte interface is predicted. | completed |
| Jun. 2017 | The effect of reaction kinetics on dendrite morphology is modeled from the implicit SEI dendrite growth model. | on track |
| Sep. 2017 | The explicit SEI dendrite growth phase-field model is established. | on track |
| Dec. 2017 | Determine if the effect of SEI on dendrite growth should be modeled implicitly or explicitly (GO/NO-GO) | on track |

# *Multiscale Modeling and Experimental Approach*

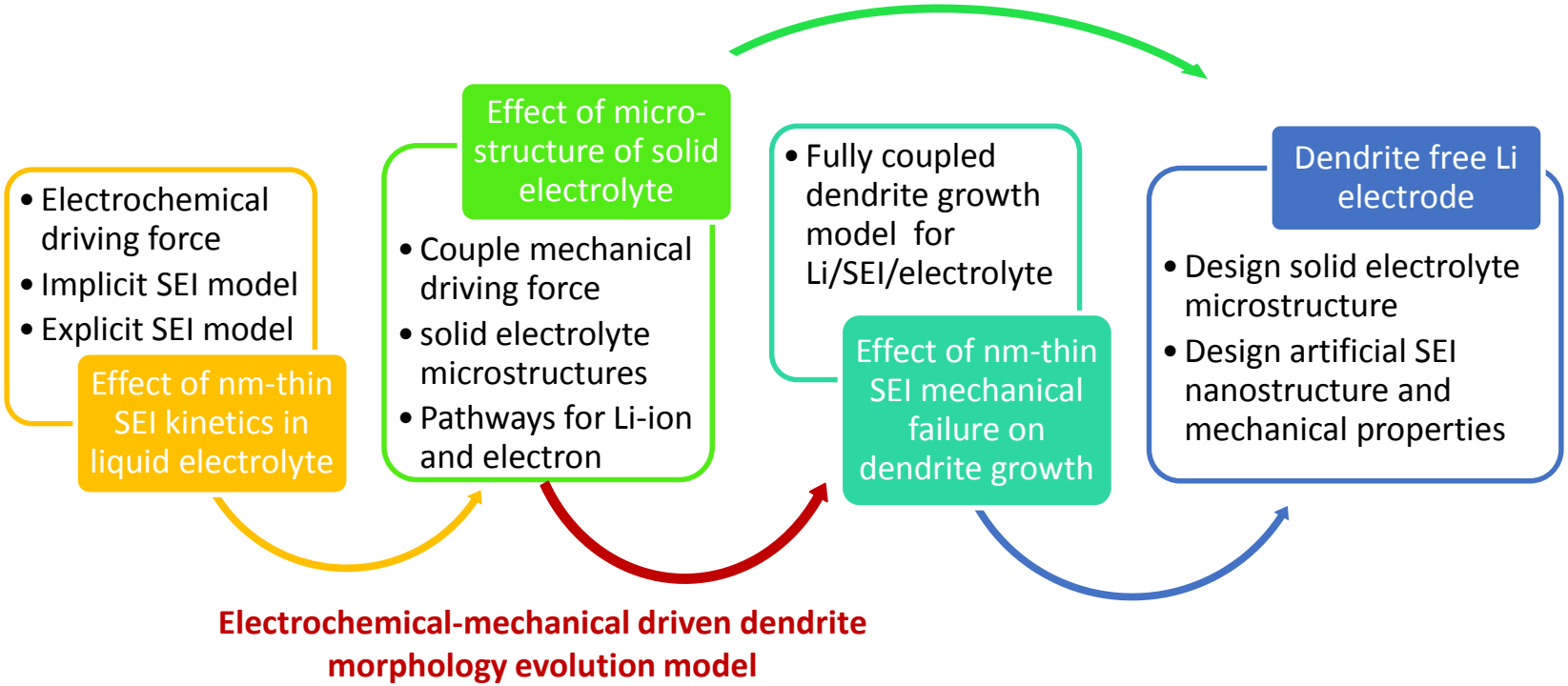
- **Formulate** a general framework that captures the electrochemical-mechanical driving forces for Li morphology evolution.
- **Consider** the role of the *nm-thin SEI* in liquid-electrolytes as well as the microstructures of *μm-thick* solid-electrolytes for Li morphology evolution.
- **Connect** micron-scale phase-field models and atomic-scale DFT-based simulations via parameter- and relationship-passing in order to predict *Li dendrite nucleation and growth kinetics and morphology*.
- **Validate** the key input parameters and main conclusions of the multi-scale model as new capabilities being developed step-by-step.



# *Model Development Strategy and Timeline*

Model liquid and solid electrolytes in order to couple electrochemical-mechanical driven dendrite growth step-by-step



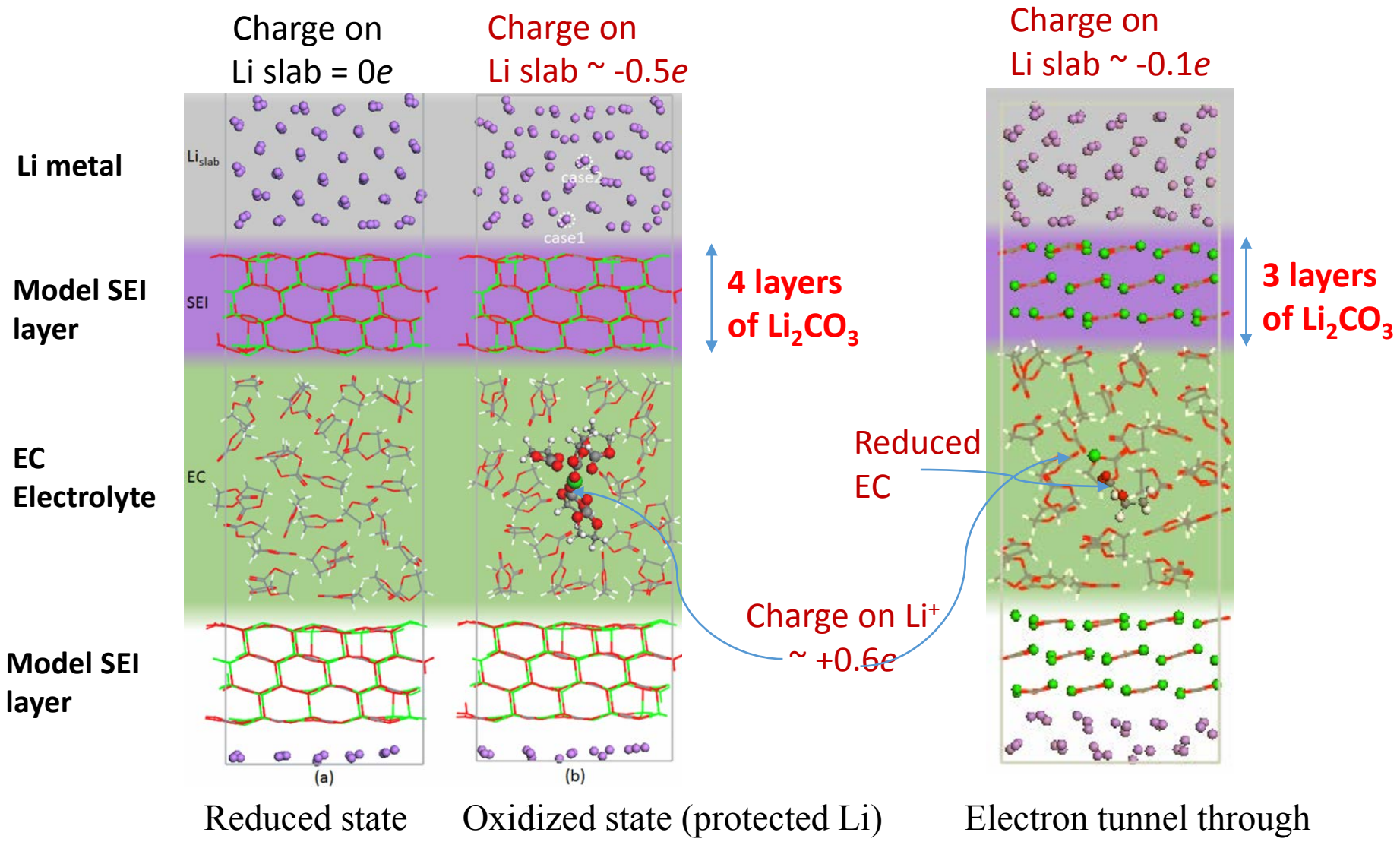
# *Accomplishment 1: Developed DFTB models to predict the reaction energy and kinetics of Li ion transporting through the SEI layer*

Density Functional Tight Binding (DFTB) merges the reliability of DFT with the computational efficiency of tight binding, becoming a more appropriate method for Li/SEI/electrolyte interface with more than 1000 atoms.

## *Accomplishment 1a: Finished DFTB parameterization*

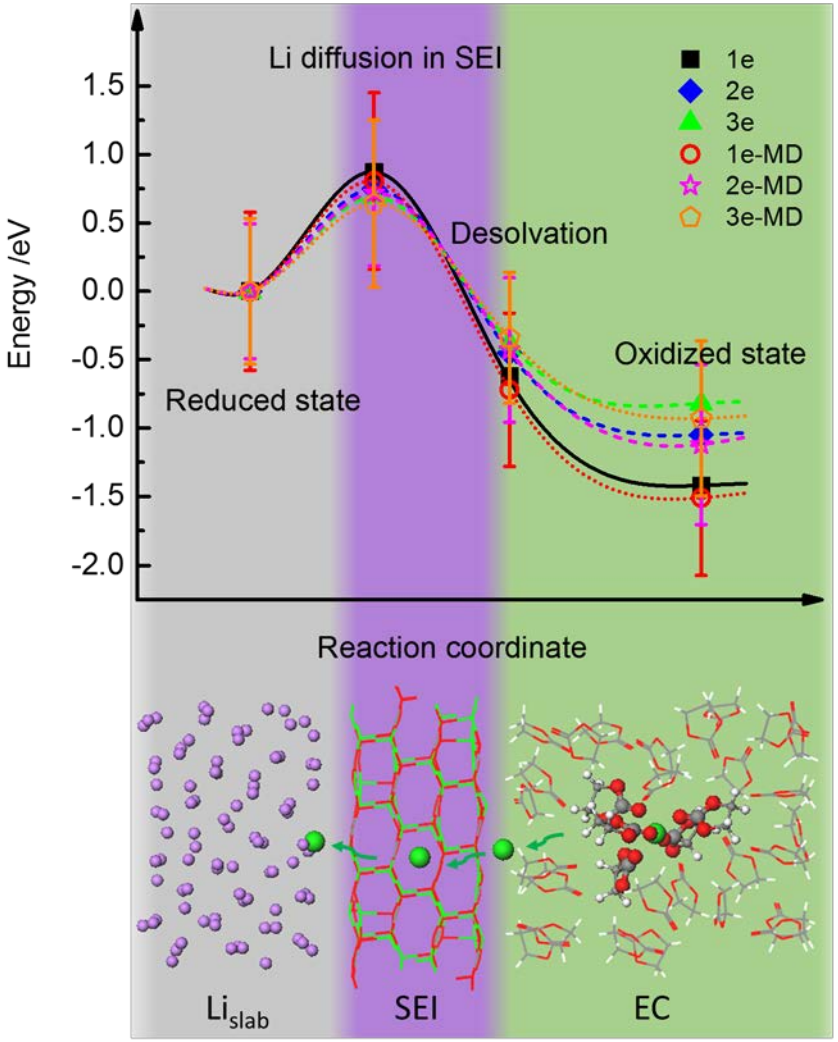
- Obtained the a new set of DFTB parameters for Li, H, C, O interactions by fitting to DFT results of a broad range of structures (BCC, FCC and HPC Li metal, $Li_2O$, LiOH, LiH, $LiCH_3$ and $LiC_6$), surface energy, adsorption energy, band structures.
- Validated the new set of DFTB parameters for Li, H, C, O interactions by comparing to additional DFT results
  - HOMO and LUMO gap of EC molecules is 7.6eV ( 7.9 according to DFT )
  - Interface energies of $Li/Li_2CO_3$ as 0.50 $J/m^2$ (0.64 $J/m^2$ according to DFT)
  - $Li^+$ solvation energy in EC as 5.4 eV (5.2~5.5 eV according to DFT)
  - Li diffusivity in liquid EC at 450K as $2.4x10^{-5}$ $cm^2/s$ ($1.1x10^{-5}$ $cm^2/s$ AIMD)

# *Accomplishment 1: Developed DFTB models to predict the reaction energy and kinetics of Li ion transporting through the SEI layer*




# *Accomplishment 1b: Captured the effect of $Li_2CO_3$ in preventing EC decomposition*

# *Accomplishment 1: Developed DFTB models to predict the reaction energy and kinetics of Li ion transporting through the SEI layer*




- ✓The energy difference of the oxidized states relative to the reduced state decreases with the applied potential (electron density on Li metal slab).
- ✓ The $Li^+$ ion dissolvation barrier and charge transfer reaction energy barrier decrease with the applied potential (electron density on Li metal slab).
- ✓The calculated average energy from MD is close to that from minimization with the maximum deviation of 0.1eV.
- ✓The energy landscape will be inputted into the phase field model

***Accomplishment 1c: Predicted the Energy Landscape for an $Li^+$ transporting through an SEI layer (4 layers of $Li_2CO_3$)***

# *Accomplishment 2: Developed an implicit SEI dendrite growth model to study the effect of SEI properties on dendrite morphology*

The nano-meter thick SEI layer plays a crucial role in Li electrodeposition.

The effects of SEI is implicitly taken into account by parametric study of the metallic Li/liquid electrolyte binary phase field model.

***Accomplishment 2a: Coupled phase filed model with the SEI properties computed from DFT and DFTB calculations.***

Diffusion equation:

$$\frac{\partial \tilde{c}_+}{\partial t} = \nabla \cdot \left[ D^{eff} \nabla \tilde{c}_+ + \frac{D^{eff} \tilde{c}_+}{RT} nF \nabla \phi \right] - \frac{c_s}{c_0} \frac{\partial \xi}{\partial t}$$

Evolution equation:

$$\frac{\partial \xi}{\partial t} = -L_\sigma \left( g'(\xi) - \kappa \nabla^2 \xi \right) - L_\eta h'(\xi) \left\{ \exp\left[ \frac{(1-\alpha) nF \eta_a}{RT} \right] - \tilde{c}_+ \exp\left[ \frac{-\alpha nF \eta_a}{RT} \right] \right\}$$

DFTB results

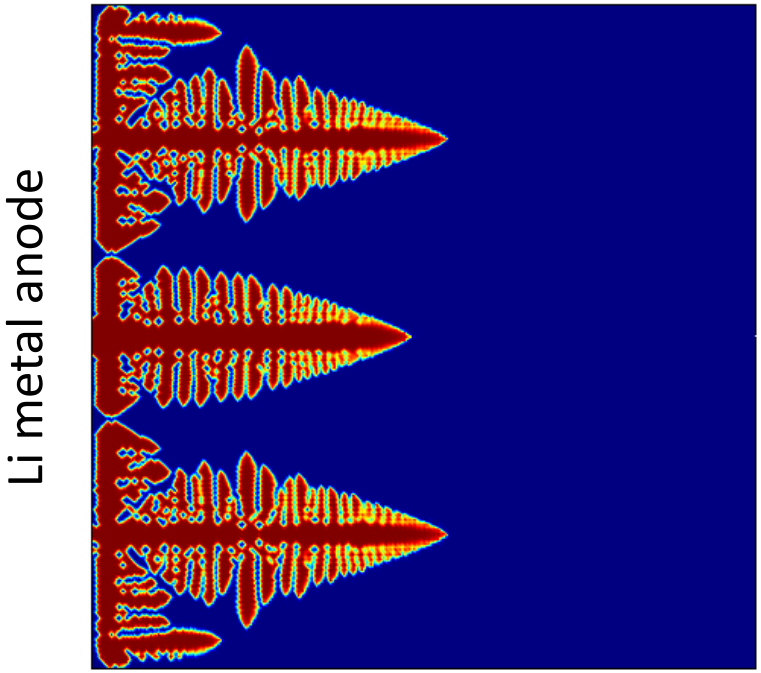
SEI effects on Butler-Volmer kinetics $L_\eta (k_0)$

Summary of LiF and $Li_2CO_3$ properties from DFT calculation

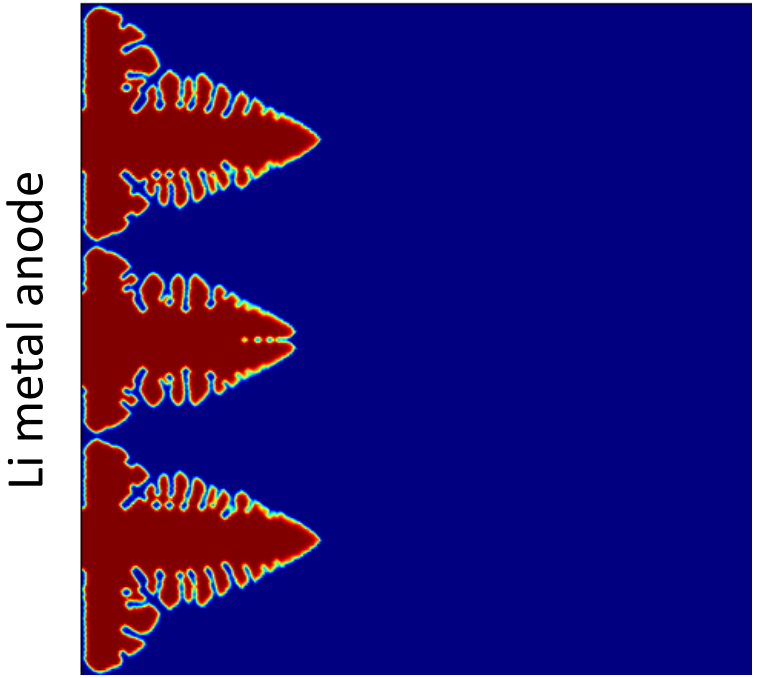
| SEI material | Interfacial energy (to Li metal) | Anisotropy | Li ion diffusion coefficient | Charge transfer rate |
|---|---|---|---|---|
| LiF | high | small | low | low |
| $Li_2CO_3$ | low | large | high | high |

# *Accomplishment 2: Developed an implicit SEI dendrite growth model to study the effect of SEI properties on dendrite morphology*

DFT calculation inputs: interfacial energetics, anisotropy, Li ion diffusion coefficients, charge transfer rate and double-well energy profile




$Li_2CO_3$ as SEI: mossy Li dendrite



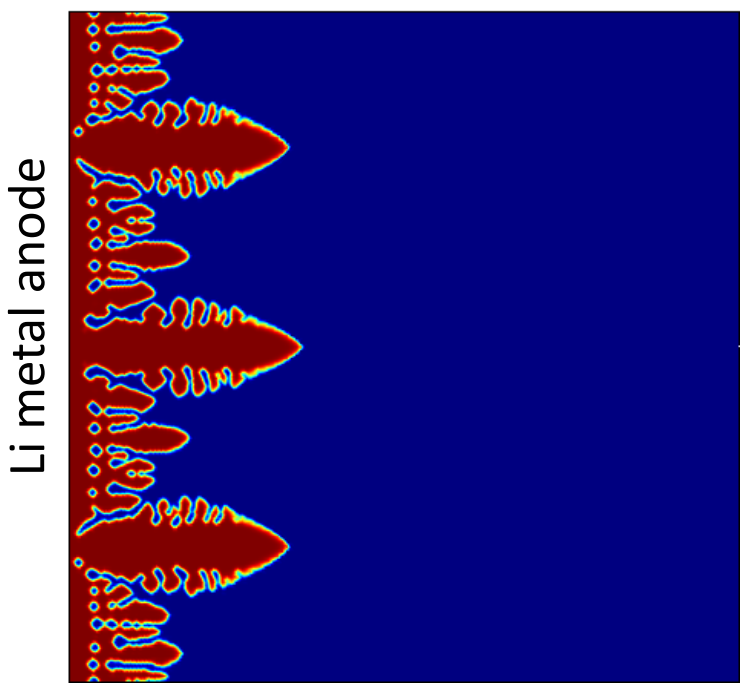

LiF as SEI: chunky Li dendrite

***Accomplishment 2b: Clarified that charge transfer rate constant plays a more dominating role on the plating morphology than other parameters.***

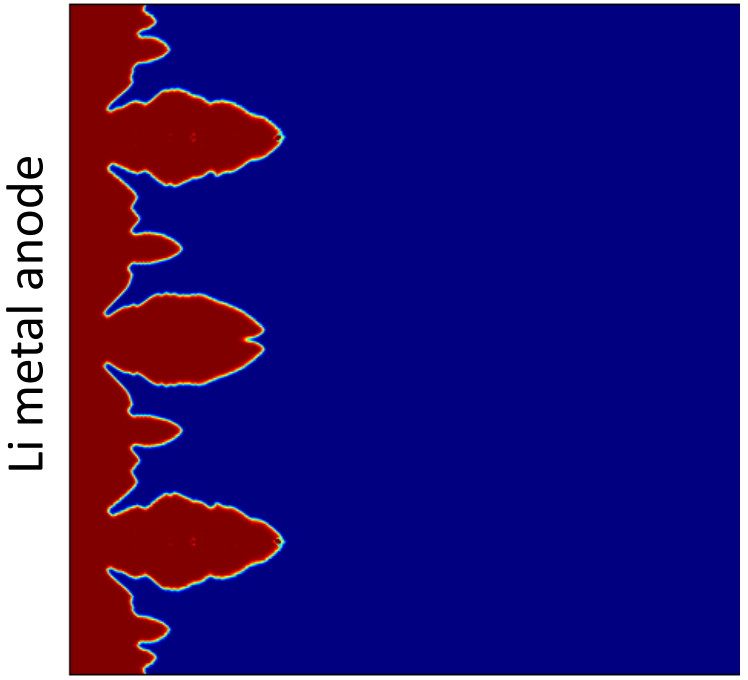
***(no mechanical coupling yet)***

# *Accomplishment 2: Developed an implicit SEI dendrite growth model to study the effect of SEI properties on dendrite morphology*

DFT calculation inputs: interfacial energetics, anisotropy, Li ion diffusion coefficients, charge transfer rate and double-well energy profile




Low Li atom surface diffusion

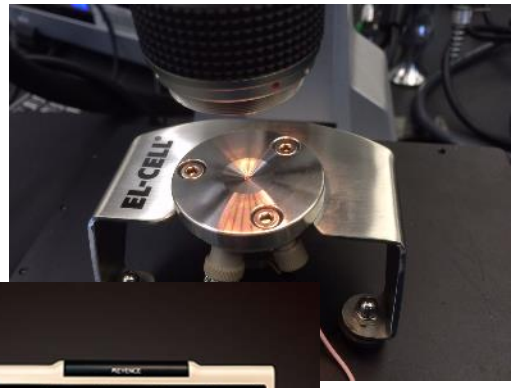



High Li atom surface diffusion

***Accomplishment 2c: Clarified that low Li atom surface diffusion can lead mossier morphology near Li surface and the growth model is at the tip rather than from the root. (no mechanical coupling yet)***

# *Accomplishment 3: Established the in-situ experimental techniques and validation plan to validate the model in liquid electrolyte*

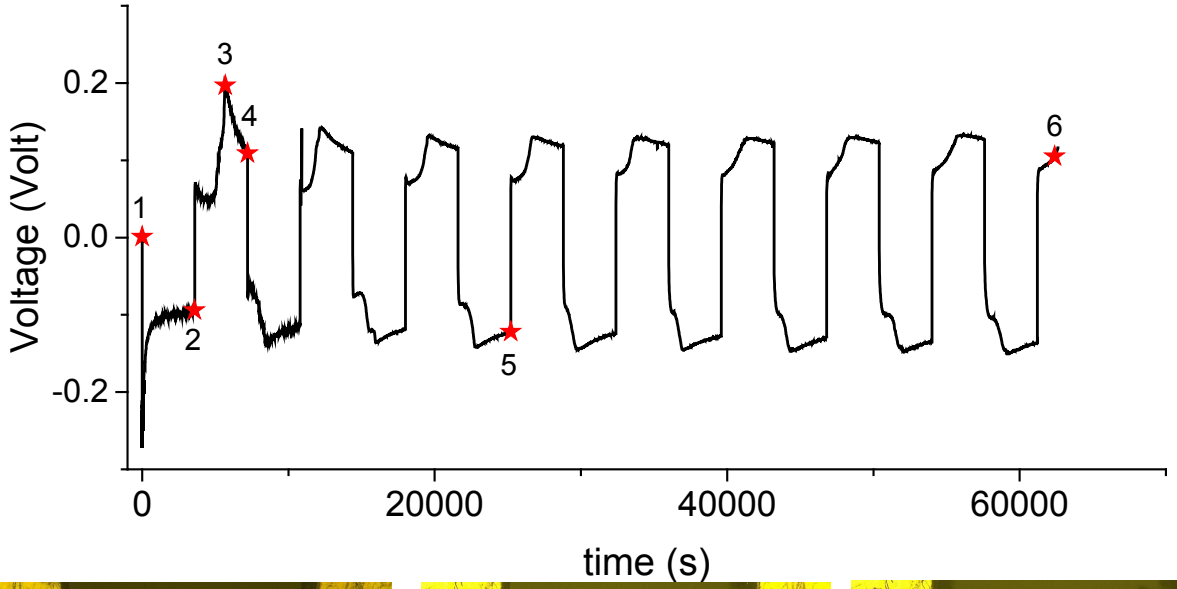
- Demonstrated that the integrated PVD and glovebox can prepare well controlled model system:
  - Li film electrode with well-controlled capacity (thermal evaporation)
  - Different coating materials
- Developed in-situ techniques to study the dendrite growth morphology and dynamics with the digital image correlation approach.
- Explored the impact of some critical charge/discharge parameters including the current density.

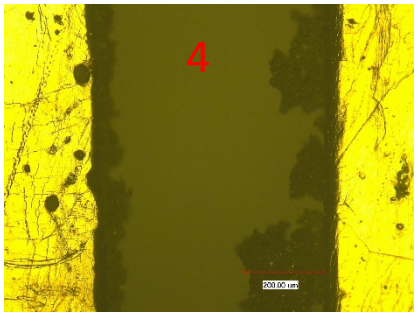


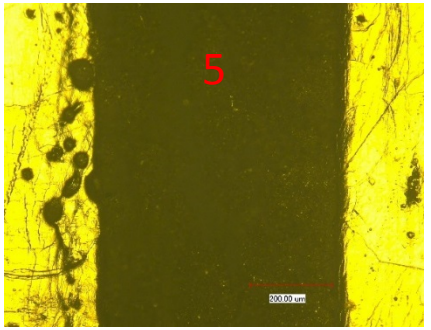

# *Accomplishment 3: Established the in-situ experimental techniques and validation plan to validate the model in liquid electrolyte*

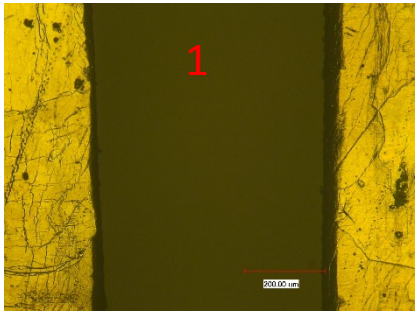
## Direct observation of dendrite and mossy structure evolution

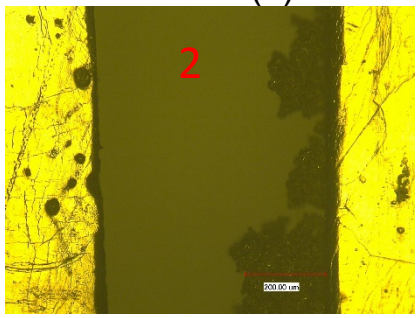
in-situ electrochemical optical observation shows the Li plating and stripping process which involves dendrite and mossy structure formation.

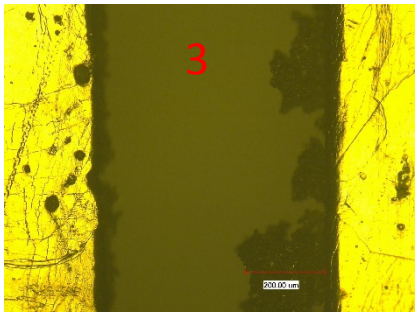


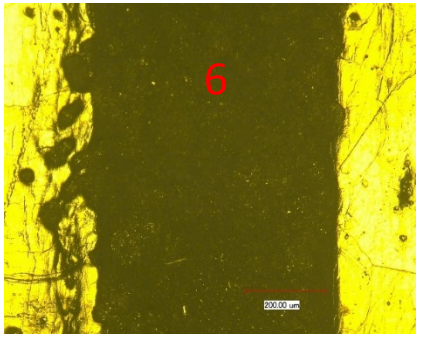



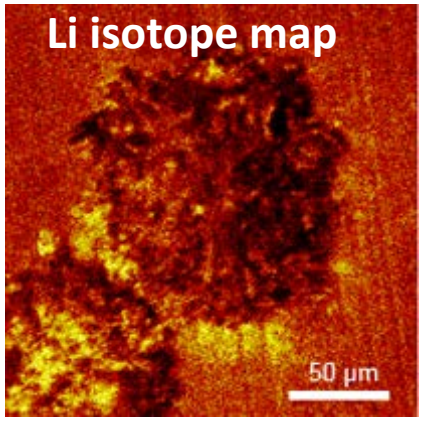



# *Accomplishment 3: Established the in-situ experimental techniques and validation plan to validate the model in liquid electrolyte*

**Validation Plan to correlate the SEI transport properties with Li dendrite formation**:




- Deposit nm-thick artificial SEI composed of $Li_2CO_3$, LiF, $Li_2O$, $Li_3N$ on Li file electrode.
- Vary the composition and nanostructure to control different transport properties
  - *For example: $Li_2CO_3$ has faster Li ion transport property than LiF but LiF is a better electron insulator, which property will determine Li dendrite growth morphology?*
- Correlate the transport properties of inorganic SEI compounds with Li dendrite morphology and compare the trend with modeling.
- Identify the critical parameters responsible for dendrite growth, establish a design map for SEI or protective coating.

# *Responses to Previous Year Reviewers' Comments*

**New project started on 1/1/2017.**

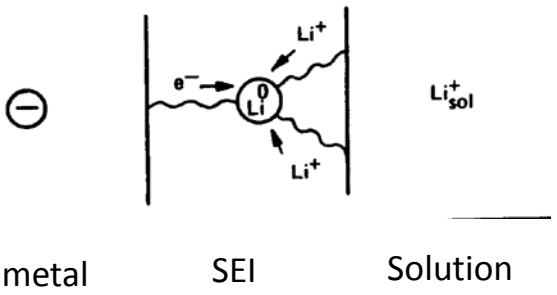
**Not reviewed last year.**

# *Collaboration and Coordination with Other Institutions*

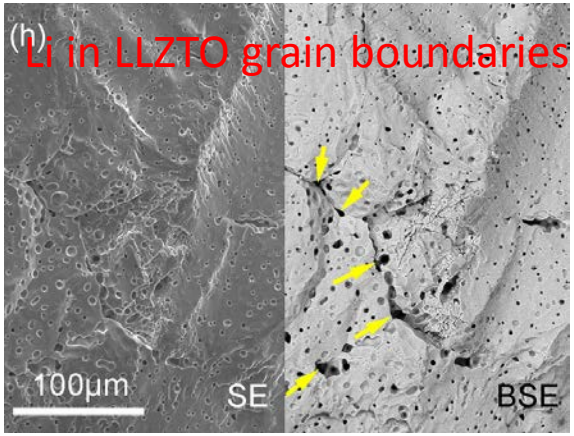
| | |
|---|---|
| **Gary Rublof**<br>University of Maryland<br>(DOE NEES EFRC) | Apply ALD LIPON coating, which has higher Li conductivity compared to typical SEI components, such as (LiF, $Li_2O$, $Li_2CO_3$), so the thickness and mechanical compliance of the artificial SEI can be investigated. |
| **Katherine Jungjohann**<br>SNL-ALBQ<br>(DOE NEES EFRC & CINT) | Investigate the Li morphology using sealed liquid cell for in situ scanning transmission electron microscopy (STEM), and investigate the effect of artificial SEI coating on morphology at nano-meter scale . |
| **Jie Xiao**<br>PNNL and U. Arkansas | Investigate the effect electrolyte additives and their role on SEI. |

# *Remaining Challenges and Barriers*

- What is the correlation of SEI transport and mechanical property with Li dendrite morphology?
- How to obtain accurate properties of SEI?
- Why and how does Li grow through the mm thick solid electrolyte?
- Can we avoid Li dendrite growth in solid electrolyte by microstructure design?
- Can we take the solid electrolyte microstructure design idea into nm-thick artificial SEI design?




***E. Peled,*** *Lithium batteries, edited by Jean-Paul Gabano. **198**3, Publisher: London, Academic Press,*




*Y. Ren et. al, Electrochemistry Communications 2015, 57, 27*

# *Proposed Future Research*

- Correlate SEI properties with Li dendrite morphology in liquid electrolyte
- Develop an explicit SEI dendrite growth model to capture the internal structures of SEI.
- Investigate the electrochemical-mechanical-structural coupling effects and explore the mechanism of Li dendrite formation in solid electrolytes from phase field model
  - calculate the electron and ion transport pathways for Li-metal growth in garnet from DFT-based methods.
  - incorporate the mechanical and electrochemical driving forces for Li dendrite growth in solid electrolytes.
  - experimentally vary the microstructure and porosity of solid electrolytes and observe the corresponding dendrite morphology.

***Any proposed future work is subject to change based on funding levels.***

# *Conclusions*

- Established a multi-scale modeling frame work and an experimental validation procedure to capture the role of SEI and solid electrolyte microstructure in Li dendrite morphology modeling.
- Developed DFTB models to predict the reaction energy and kinetics of Li ion transporting through the SEI layer
  - *Finished DFTB parameterization*
  - *Captured the effect of $Li_2CO_3$ thickness in preventing EC decomposition*
  - *Predicted the Energy Landscape for an Li+ ion transport through an SEI layer (4 layers of $Li_2CO_3$)*
- Developed an implicit SEI dendrite growth model to study the effect of SEI properties on dendrite morphology
  - *Coupled phase filed model with the SEI properties computed from DFT and DFTB calculations.*
  - *Clarified that charge transfer rate constant plays a more dominating role on plating morphology (without mechanical effects) than other parameters.*
  - *Clarified that low Li atom surface diffusion can lead mossier morphology near the surface and growth model is at the tip rather than from the root.*

# *Acknowledgements*


- Tien Duong and Walter (Jerry) Parker for program management.
- Dr. Yunsong Li, Zhe Liu, Yuxiao Lin, Qinglin Zhang for the modeling and experimental work.

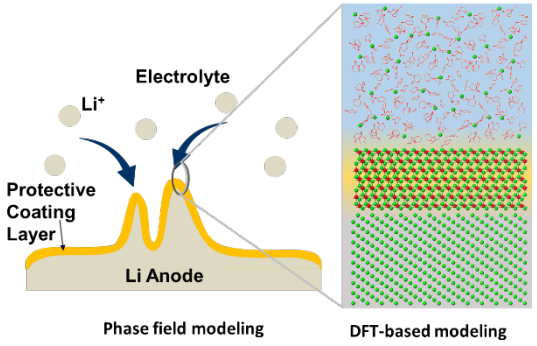
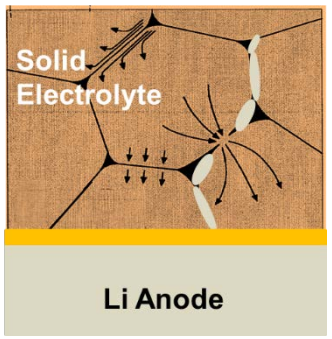
# *Publications and Presentations*

- Yue Qi, Modeling of the Interface and Interphases in Li-ion batteries, Mechanical & Materials Engineering University of Nebraska-Lincoln, March 2017 (invited seminar).
- Yue Qi, Multi-component and Multi-functional Protection coating for high capacity anodes (Li and Si), 2017 MRS spring meeting, Phoenix, AZ, April 18, 2017, (invited talk).
- Y. Li and Y. Qi, “Computational Insights to Charge Transfer Reactions at Electrode|SEI|Electrolyte Interface”, 2017 MRS spring meeting & exhibit, Phoenix, AZ, April 20 2017.
- Z. Liu, L. Chen, Y. Qi, P. Lu, X. Xiao and L. Q. Chen, "A non-linear Multi-phase field model for Li plating and dendrite growth at Li metal anode incorporating solid electrolyte interphase (SEI) layer", 231th ECS meeting, New Orleans, LA, May 30 2017.

# *Technical Back-Up Slides*

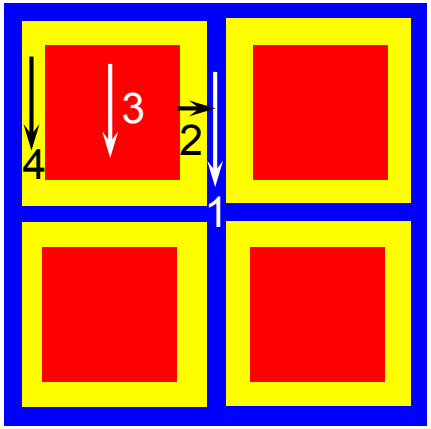
# *Technical Back-Up Slides*

## *Compare liquid and solid electrolyte to understand the role of SEI in dendrite growth*

| | Growing in liquid electrolytes | Growing in solid electrolytes |
|---|---|---|
| **Knowledge Transfer** | → The effect of the nm-thick protective SEI layer (exist in both)<br>The effect of the microstructure (easier for experiment ) ← | |
| **Key phenomena** |  |  |
| **Key questions** | The effect of the nm-thin SEI<br>The relationship with the separator porous and mechanical structure | The growth mechanism in mm-SE.<br>Mechanical confinement from the pore and weak interfaces in SE. |
| **Common** | Common components in the SEI at Li/electrolyte interface: such as $Li_2O$ | |
| **Similar situations** | Polymer electrolyte at high temperature (T) | polymer electrolyte at low T |
| **Different Atomistic Details** | $Li^+$ and e Transport at the Li/SEI/liquid-electrolyte interface | $Li^+$ and e transport at the SE surface and boundaries |
| **Phase-field model similarities** | Governing equations, Butler-Volmer kinetics, Charge carrier (electron and Li-ion) transport, include microstructure details, track microstructure evolution | |

# *Technical Back-Up Slides*

## *Phase field model can incorporate the microstructure influence on ionic conductivity and Li dendrite morphology*

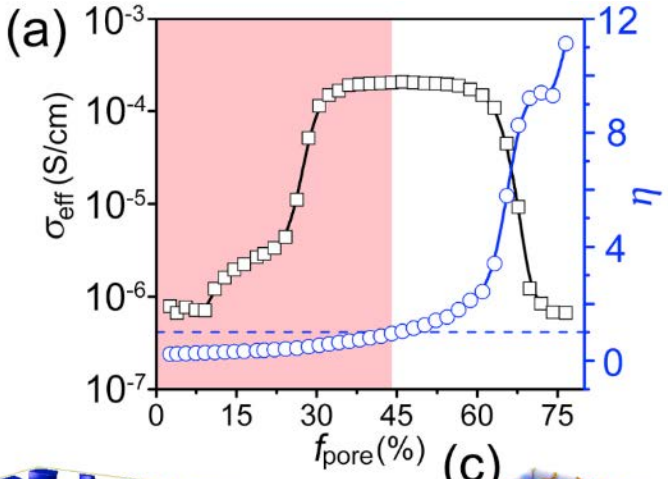


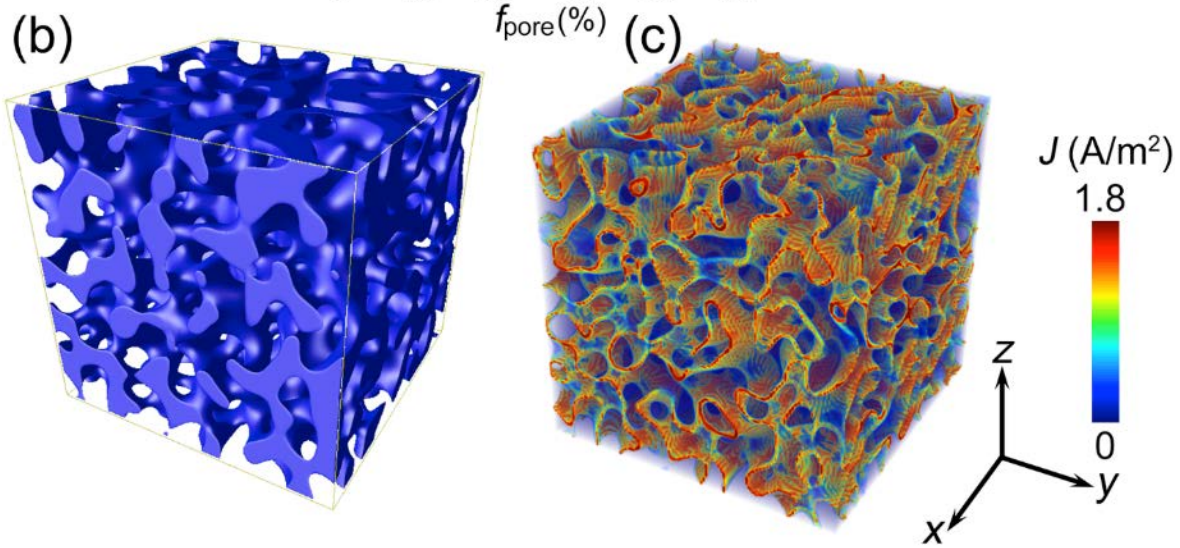

Bulk

Space-Charge Zone

Grain Boundary Core

The effective Li-ion conductivity ($\sigma_{eff}$) and mechanical stability factor ($\eta$) as a function of pore phase fraction (fpore)




- How can we obtain thermodynamics and transport properties at pore surface and space charge zone?